

# **Report as of FY2010 for 2010PA125B: "Predicting Total Mercury in Pennsylvania Soils in Order to Predict Pennsylvania Watersheds with the Highest Total Mercury Contents "**

## **Publications**

- Dissertations:
  - ◆ Erich, Emilie, 2010, Pedogenic fate and transport of total mercury across subaerial and subaqueous soils in an Appalachian Plateau impoundment, M.S., Crop and Soil Sciences Dept., Penn State University, University Park, PA, 260 pp.
- Articles in Refereed Scientific Journals:
  - ◆ Erich, E., P.J. Drohan, R.L. Ellis, M.E. Collins, M. Payne, D. Surabian. 2010. Subaqueous soils: their identification and importance in ecosystem management. Soil Use and Management 26:245-252.

## **Report Follows**

## PROJECT TITLE & PRINCIPAL INVESTIGATOR

Predicting total mercury in Pennsylvania soils in order to predict potential stream Hg loading.  
Patrick Drohan and others, Department of Crop and Soil Sciences, Pennsylvania State University

## PROBLEM & RESEARCH OBJECTIVES

Regional, mercury (Hg) emitting, coal-fired power plants, manufacturing and waste incineration, along with high amounts of annual precipitation, result in Pennsylvania receiving some of the heaviest loads of atmospheric Hg deposition in the United States. While much research has examined Hg accumulation in water bodies, there has been limited assessment of Hg accumulation in soils, especially over a great aerial extent and with depth. This proposal addresses the identified gap in knowledge by examining atmospheric deposition loads and soil Hg contents across Pennsylvania, in order to identify watersheds at greatest risk to Hg pollution.

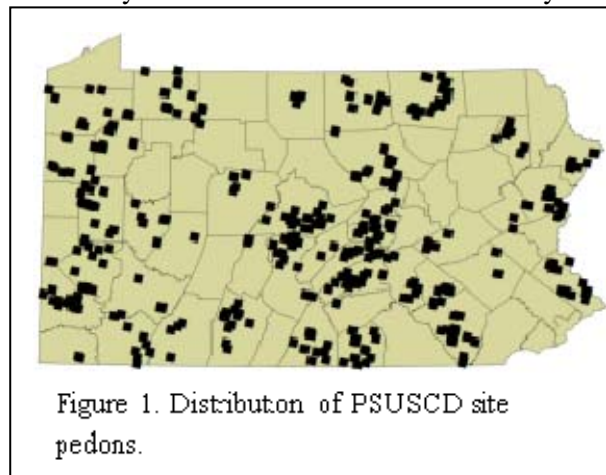
## METHODOLOGY

### Objective 1: Derive soil Hg loading across Pennsylvania Benchmark soils

The USDA-NRCS Soil Survey program has identified specific soil series in the United States as Benchmark soils. A benchmark soil is: one of large extent within one or more major land resource areas (MLRA); has a large amount of soil physical, chemical, and mineralogical data; has special importance to one or more significant land uses; or is of significant ecological importance (USDA-NRCS, 2009). In completing Objective 1, we will use archived Benchmark soil series pedons and associated archived characterization data from the Penn State Soil Characterization Database, to develop soil loadings, base line critical concentration estimates for Hg in Pennsylvania Benchmark soil series, and to identify watersheds potentially prone to heavy Hg-loading.

Because the archived pedons represent a point in time approximately 30 years ago, our calculation will represent base line data and thus be extremely useful to future users of soil survey data in comparing Hg accumulation in soils over time. Hg-T analysis of full pedons will also provide us with an estimate of parent material Hg contributions; parent material Hg contributions are very poorly understood in the Northeast U.S.

*Methods.* Twenty one Benchmark series occur in Pennsylvania. In the Penn State Soil Characterization Database (PSUSCD [Ciolkosz and Thurman, 1992]), nineteen of these series have archived pedons (139 total pedons [Figure 1], 1086 horizons: Berks (13 pedons); Brinkerton (4); Buchanan (8); Cavode (9); Clarksburg (10); Clymer (5); Duffield (9); Ernest (8); Gilpin (4); Hazleton (17); Lackawanna (10); Leck Kill (10); Morris (5); Penn (5); Readington (5); Weikert (2); Westmoreland (4); and Wharton (3).



These series represent dominant Pennsylvania parent materials:

1. limestone (10 pedons);
2. argillaceous limestone (9);
3. gray and brown acid sandstone (30);
4. gray and brown acid shale (40);
5. calcareous shale (4);
6. acid till (13) and
7. red acid shale (33).

Eight of the series have fragipans and the series distribution spans drainage classes from poorly drained to well drained. Eight pedons were sampled after 1973 but before 1983; remaining pedons were all sampled prior to 1973.

Hg-T will be measured via a Milestone DMA-80 Direct Mercury Analyzer (EPA method 7473 protocol [US EPA 2000]). Analysis will be completed by the Penn State Institutes of Energy and the Environment (PSIEE) water quality laboratory, University Park, PA under direction of collaborator Dr. Elizabeth Boyer. Archived profile data (horizon thickness and bulk density (available for each horizon)) will be used to derive soil Hg contents, and existing soil horizon physical, chemical and mineralogical data will be used in conjunction to develop Benchmark series representative regression relationships to predict Hg-T content in soils throughout state. Using results from previous soil-related Hg research as a guide for variable analysis (Aastrup et al., 1991; Lindqvist et al., 1991; Hultberg et al., 1995; Schwesig et al., 1991), we will specifically examine Hg-T vs.: soil profile morphology (sub-horizon type, redoximorphic feature presence; depth and thickness); bulk density; particle size trends (sub-fractions too); Total N; cation exchange capacity; base saturation; pH; organic carbon content; Al, Fe, Mn; and XRD derived mineralogy (all parameters for every horizon are already measured and thus available for statistical analyses).

Calculations from de Vries et al. (2007) will be used to calculate Hg-T critical loadings for soil horizons. C-horizon Hg-T data will be statistically compared across parent materials using a non-parametric Kruskal Wallace multiple comparisons analysis (Minitab, 2005) to assess natural Hg-T in soils. In addition, similar comparisons will be made for surface horizons to infer atmospheric deposition loadings representative for the time of sampling.

*Expected Outcome.* Objective 1 allows us to take advantage of the 30+ years of archived Soil Survey pedon data and extend soil survey interpretations for Pennsylvania to include Hg-T. These calculations will assist us in evaluating statewide Hg loading developed in Objective 2 and provide an extremely valuable future data set for Hg monitoring in the Northeast. This methodology will allow us to evaluate hypotheses one and three while also helping pose new hypotheses. Results from Objective 1 will be used to present one refereed journal article on Hg-T trends across Pennsylvania Benchmark series, parent materials, and drainage classes and provide valuable data for future research proposals.

*Objective 2. 2. Develop models of Hg loading for Pennsylvania soils and identify watersheds with potentially high Hg loadings.*

Benchmark soil series Hg-T contents developed in Objective 1 will be used to develop three soil Hg content models for PA Benchmark soils.

First, a *surface horizon's model* will be developed using surface O and A horizon data and second a *parent material model* will be developed using C horizon data. These two models will provide a base line approximation of soil Hg-T across Pennsylvania. These two soil models will then be coupled with existing Hg deposition data provided by collaborator Dr. Elizabeth Boyer, to construct a *Hg critical loading model* across the state for all soils using the digital Statewide Soil Geographic Database (SSURGO).

*Methods. Mercury deposition data:* Hg deposition data will be provided by the Pennsylvania Atmospheric Deposition Research Program, led by Dr. Elizabeth Boyer. Boyer and colleagues have monitored wet atmospheric Hg deposition weekly in Pennsylvania since 2000 to quantify spatial and temporal patterns of Hg and to understand consequences of Hg emissions in the atmosphere (Boyer et al. 2009). Boyer operates 9 sites at present in PA (with 2 additional planned for 2010), all of which are contributed to the National Atmospheric Deposition Program's Mercury Deposition Network (MDN). Both measured data (from the point monitoring locations) and modeled data (see below) will be developed for use in our state-wide model of accumulation of Hg in soils (Figure 2). Where needed for spatial analysis, the ArcGIS platform will be used.

*Model development and data delivery:* We will first develop a map of contemporary wet atmospheric Hg deposition at high resolution across Pennsylvania (quarterly and annually), using a modification of methods put forth by Grimm and Lynch (2004) and Golden and Boyer (2008). A statistical model is developed that combines detailed spatial and topographic data with precipitation observations from a dense network of rain gage stations to produce high-resolution estimates of precipitation across PA. This in turn is combined with the monitoring data of Hg in precipitation from the Pennsylvania MDN sites, producing estimates of wet deposition that have been shown to be more accurate than those obtained using traditional two-dimensional interpolation algorithms (Grimm and Lynch 2004).

Dry Hg deposition is not operationally measured at the MDN sites (in PA or nationwide), and thus we will estimate the dry component of Hg deposition throughout PA on the basis of the wet deposition, imposing ratios of dry/wet deposition that are simulated from a simulation model.

We will quantify ratios of dry/wet deposition across PA using contemporary Hg simulations from NOAA/EPA's Community Multiscale Air Quality model, under current base scenarios (Bullock & Brehme 2002). Our resulting high-resolution maps of total (wet + dry) Hg deposition in Pennsylvania will be used as a proxy for Hg loadings to soils across Pennsylvania. Using data from Objective 1 and 2, Critical Concentrations for all soils in the state will be estimated on the basis of the pedogenic characteristics.

Last, in collaboration with Dr. Anthony Buda of the USDA-ARS and Dr. Elizabeth Boyer, model results of soil Hg loading, in conjunction with State Soil Geographic (SSURGO) digital soil data, will be used to develop Hg loadings for all soils in Pennsylvania. Using identified relationships between soils and Hg-T developed in Objective 1, we will model Hg-T for other soils in the SSURGO database not analyzed in our research. We will then use our soil loadings in conjunction with a dataset of Pennsylvania watersheds [9,895 watersheds] (PADER/USGS, 1989; Seaber, 1987) to identify watersheds at the greatest risk of Hg-T loading (natural and anthropogenic). Natural loadings will be considered derived from soils in our model where parent material contributions are high.

#### *Expected Outcome.*

We will construct a statewide assessment of potential Hg loading to soils and watersheds in Pennsylvania. We believe this will be the first model to attempt such an analysis over a geographic area the size of Pennsylvania. This methodology will allow us to further evaluate hypotheses one and three and evaluate hypothesis two. In addition, this research will help us pose new hypotheses.

The accessibility of the model to others will insure ease of availability and maximize usefulness for future research. Results from this objective will be combined into two refereed journal articles: one on Hg-T soil critical loading across Pennsylvania and one on watershed loading. Results from this objective will also provide valuable data for future research proposals.

Our models of probable Hg accumulation, and the associated soils at risk to Hg critical loading will be *first approximations* -- limited by the available data, and are affected by vast heterogeneity in Hg in the air (sources, emissions, transport, deposition) and on the landscape (terrain, soils, wetness, etc). We will urge appropriate caution with regard to the utility and interpretation of the results. However, this will be the first attempt at statewide projections of Hg risk, and our results will be useful at generating interest

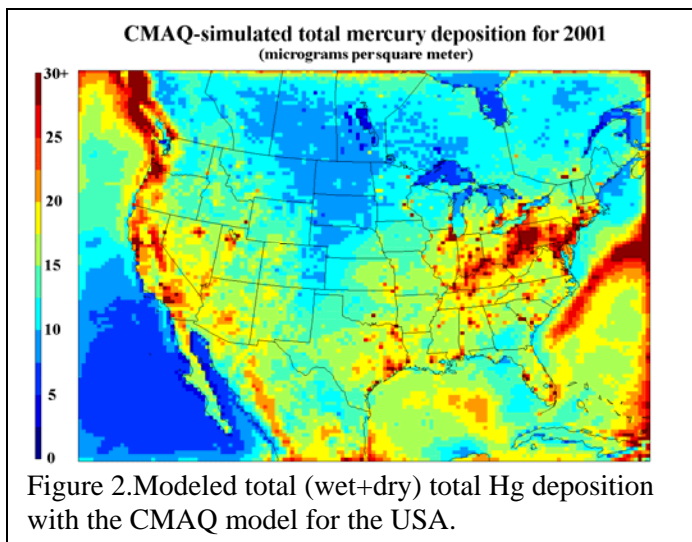
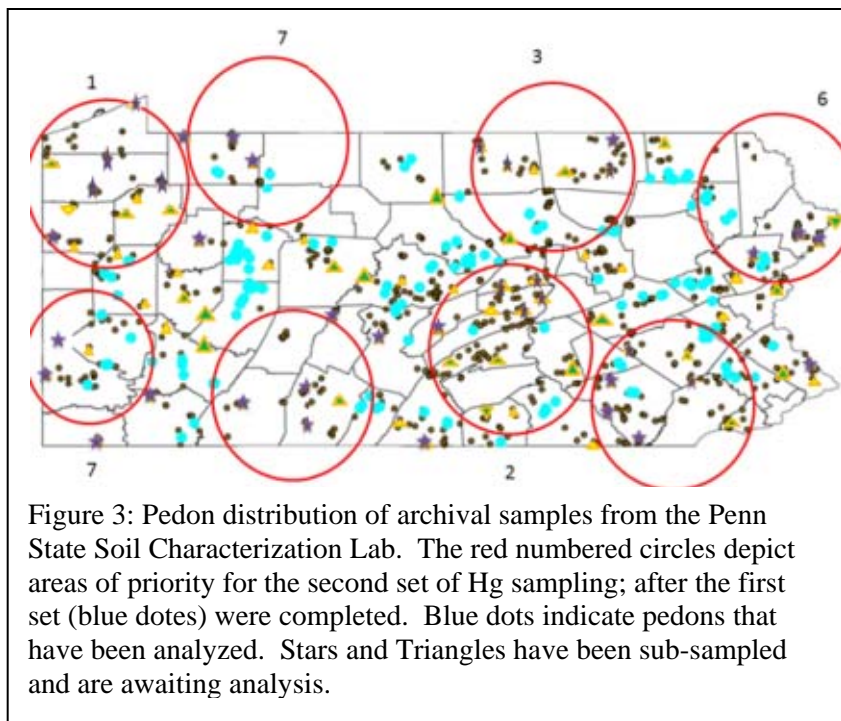


Figure 2. Modeled total (wet+dry) total Hg deposition with the CMAQ model for the USA.

in the problem and will generate *testable* hypotheses about the accumulation of Hg in soils of Pennsylvania that can be followed in subsequent studies.

## PRINCIPAL FINDINGS AND SIGNIFICANCE

While statewide analysis is still being conducted some results are available. To date a total of 1441 horizons from 194 pedons have been sub-sampled for Hg analysis by a Direct Mercury Analyzer from Milestone Inc (model DMA-80). Samples were determined by availability and spatial distribution. Sampled soil orders include pedons from 74 Inceptisols, 54 Alfisols, 64 Ultisols, 2 Entisols, 1 Spodosol, and 1 Mollisol. Of these horizons, 975 have been analyzed thus far. Subsoil total Hg contents range from 10.7 to 470 ng/g; the highest surface horizon value found was 420 ng/g. Pedons sub-sampled for this study were initially sampled across the state in a time frame ranging from 1957-1984 (Figure 3).



A regional analysis has been completed on a local watershed at Black Moshannon Lake. In this sub-study total Hg sequestration appears to be greater in upland soils where both the surface horizon and subsurface horizons retain Hg. The Cookport soil series has the greatest total Hg pool, and generally does not border Black Moshannon Lake or areas with water tables less than 50 cm. However, this observation bodes poorly for the health of Black Moshannon Lake because the smaller pool of total Hg in the Nolo series and subaqueous soils in the lake is likely due to subsurface transport from the Cookport to the Nolo, and a loss of Hg from subaqueous soil Oe horizons via methylation. Though the Nolo series retained some total Hg in the surface horizon, both content and pools were low in subaqueous soils. This indicates that drainage and the downslope redirection of subsurface flow by a fragipan are two key controls on Hg transport.

Above a fragipan, redoximorphic features (RMFs) were found to be present, with Fe and Mn mineralogies and associated soil organic carbon (SOC) that can tightly bind Hg. In Black Moshannon Lake soils, the pattern between RMFs, SOC, and Hg distribution is still unclear, but it appears that RMFs may be short-term micro sinks and long-term source with intermittent saturation via water table fluctuation. The surface and subsurface Hg that is delivered to the subaqueous soil profile is likely very quickly lost with particulate matter or by chemical transformation. Black Moshannon Lake appears to be an environment in which Hg methylation is likely to occur. Since the Cookport series has the greatest total Hg pool, limiting disturbance in the Cookport series will perhaps limit Hg transport. Better infiltration to improve soil drainage in the Nolo soils may reduce methylation and subsurface transport to SASs. However, increased drainage will limit carbon sequestration potential, and perhaps upset the balance of the Black Moshannon Lake wetland system.



Soil organic carbon and Hg were not always correlated in transport and accumulation (as was seen in the subaqueous soil surface horizon, where the SOC pool was the greatest, but the total Hg pool was small). This suggests that management for carbon sequestration is possible without total Hg sequestration. However, the lack of a clear relationship makes predicting the distribution of total Hg based on SOC unreliable. Therefore a combination of other factors must be considered such as particle size, other complexing mineralogies, vegetation type and the resultant type of soil organic matter. Results suggest that Hg transport increases with increased wetness (based on a decrease in total Hg and previously established methylation in such environments), and is perhaps controlled by overland particle and organic matter transport, and subsurface transport across a fragipan to a more poorly drained soil. Subaqueous soils, because of their inundated state, provide an excellent environment for methylation. Understanding SOC and Hg sequestration, and the controls on those processes, can now be integrated with soil cartographic representations of the Black Moshannon Lake hydrosequence resulting in a useful management tool.

#### **STUDENTS & POSTDOCS SUPPORTED**

Emilie Erich, Soil Science, M.S.

#### **PHOTOS OF PROJECT**



Emilie Erich (foreground) and Mary Kay Lupton mapping subaqueous soils at Black Moshannon Lake. Photo, Patrick Drohan.



Patrick Drohan holding a soil core used to describe subaqueous soils in Black Moshannon Lake. Photo, Patrick Drohan.